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Reclaiming Military Bases from Tungsten Takeover

By James Martin

Introduction

The Army has been using tungsten (periodic symbol: W) munitions since the 1990s, when the federal government determined that lead-based munitions posed environmental and human health issues – even when not propelled by gunpowder. However, tungsten small arms ammunition has recently been suspended due to production problems and, possibly, rising health and environmental issues.

Recent concerns have been raised over potential health hazards and increases in ground acidity at firing ranges that may have been caused by tungsten. Since lead residue was already present, accelerated corrosion of that lead could occur. This was of particular concern in areas where groundwater could become contaminated by lead corrosion.

Lead has been found to create learning disabilities in children exposed to even small amounts, as well as other human health problems. Tungsten was found in the drinking water of Fallon, Nev., site of numerous Tungsten mines, and may be linked to high leukemia rates among the region's children. Some testing has been done in the Massachusetts Military Reservation (MMR) on Cape Cod and the Army Aberdeen Proving Ground.

Such findings have since made it necessary to develop tools and techniques to identify the extent of tungsten and lead present in soil and potential impact on groundwater. One such tool, an X-ray fluorescence (XRF) analyzer, has already shown promising results in soils testing to accurately and quickly determine the amount of lead and tungsten under field conditions.

Challenges of base clean-up

In January 2000, the EPA ordered a large Massachusetts military base, Camp Edwards, to clean up contamination and remove unexploded ordnance. According to its administrative order, EPA-New England directed the National Guard Bureau and the Massachusetts National Guard to, "remove unexploded ordnance from the 14,000-acre Camp Edwards training grounds at the Massachusetts Military Reservation (MMR) on Cape Cod. The National Guard agencies were also directed to clean up contaminated groundwater, as well as contamination in soil that has not yet reached the groundwater, but threatens the aquifer."

The camp lay directly over the Sagamore Lens, a highly productive part of the Cape Cod Aquifer. Because the soil was highly permeable, the aquifer was particularly vulnerable to contamination. During the training years of 1995 to '97, 1.8 million rounds of lead ammunition were fired, including 287,000 rounds of tungsten-nylon 5.56 small arms ammunition in 1999 and 2000. With such significant amounts of spent munitions present at Camp Edwards, their cleanup promised to be a long term, large-scale project for field engineers. At the time of the EPA order, such efforts were already underway, beginning in 1998 with the recovery of lead projectiles and treatment of many of the berms.

Soil testing, portable XRF and EPA method 6200

Testing of such a site, containing contaminated soil involving large military installations, could prove time consuming and expensive. It would involve mapping suspected areas of a site, sampling the soil, bagging it, identifying the source, then sending it to an off-site laboratory for analysis using Inductively Coupled Plasma (ICP) or Atomic Absorption (AA) methods. While any given sample would be analyzed very accurately with ICP or AA methods, there would also be errors in the overall site assessment due to fewer samples being collected and analyzed. In other words, the sampling plan may not have yielded an accurate picture of the complete, 3-D contamination patterns.

On-site field screening using portable XRF analysis provided an excellent complement to laboratory analysis. Field screening allowed a fast and relatively inexpensive method to thoroughly delineate contamination patterns at the site. Operators could utilize the portable XRF device for either in-situ (i.e. tests directly on the ground) or collected, bagged samples. In either case, test results provided concentrations for 20 or more metals within seconds. Because a large volume of tests could be performed quickly, the site could be quickly scanned for contaminants and patterns, allowing informed decisions for sample collection, preparation and additional XRF or lab analysis.

The EPA recognized the value of field screening to increase sample volume (and hopefully decrease sampling errors) by publishing reference Method 6200, which it incorporated into SW-846 under the Resource Conservation and Recovery Act (RCRA) for field portable XRF analysis. The report was titled *Field Portable XRF Spectrometry for the Determination of Elemental Concentrations in Soil and Sediment.* The EPA publication SW-846, entitled *Test Methods for Evaluating Solid Waste, Physical/Chemical Methods,* represented the Office of Solid Waste's official compendium of analytical and sampling methods evaluated and approved for use in complying with RCRA regulations.

The method was applicable to various analytes as referenced in method 6200 for in-situ and intrusive analysis of soils and sediments. Generally, elements of atomic number 16 or higher could be detected and quantified by field-portable XRF. Tungsten, lead and uranium are all heavy metals ideal for portable XRF analysis.

Portable X-ray fluorescence basics

Field screening XRF tests can provide a number of benefits to such cleanup efforts, including:

• Speed of site survey, with quality assurance on results to complement lab analysis. Contaminants and other analytes of interest can be measured and evaluated.

• Reduction of overall testing time and costs. One can identify specific areas in a site for cleanup, and establish boundaries, reducing the overall effort and costs.

• Assurances of a properly completed site cleanup, so remediation contractors do not leave prematurely.

• Minimize the amount of soils with hazardous waste to be removed or processed. In situ testing on site assures only soils having hazardous wastes above limits are removed for costly disposal or processing.

A portable XRF consists of three basic components: an x-ray source, an x-ray detector, and electronics for signal processing, calculations and results display. The XRF directs a beam of x-rays at a soil sample, which are then absorbed by the atoms of the various elements and re-emitted in energy patterns unique to each element's atomic structures (i.e. characteristic X-rays). Portable XRF systems utilize X-ray tubes rather than radioactive isotopes. The tubes offer several advantages, including no NRC regulation, portability, faster results and low detection limits.

XRF analyzers use an x-ray detector, conditioning electronics and on-board PDA software to quantify various levels of elements in a sample. Detectors measure the energy of each x-ray strike, and count the total number of x-rays in discrete energy bands. The electronics and software process this information to yield concentration data for various elements in soils or other samples. The technology is in use at numerous EPA sites and sites under investigation by state environmental agencies.

Portable XRF analysis almost always yields better accuracy when samples are prepared. After an initial XRF survey involving in-situ testing, results can be used to identify areas that warrant a more careful investigation. Typically, these are areas of low contaminant concentrations, or levels near the cleanup requirements as identified by the in-situ testing. In these cases, operators often collect samples and prepare them to confirm the in-situ findings with more accurate results. Prepared samples are also ideal for laboratory analysis because they provide a direct comparison with XRF results.

XRF testing is non-destructive, allowing the same sample analyzed in the field to also be analyzed in the laboratory. For prepared-sample analysis, each sample is first prepared through sifting, grinding and homogenizing the selected soil. The samples are placed in standard test cups and analyzed with the portable XRF unit. Site-specific calibrations are not necessary as the analyzer's PDA software automatically corrects for variations in sample chemistry and density.

Field screening precautions

It is crucial for XRF operators to understand sources of error for field-screening work, particularly in-situ analysis. Method Detection Limits, or MDLs, depend on several factors, including x-ray excitation source and strength, analytes of interest, type of detector used, time to test samples, physical and chemical matrix effects, sample preparation, and interference from the spectra of other elements present. Accuracy can be greatly affected by sample preparation. Without thorough sample preparation that produces a uniform, homogeneous sample type, an analysis by XRF followed by a lab risks comparing apples to oranges. In general, in-situ testing is used for field screening, and prepared samples are generated for quantitative XRF analysis as well as laboratory confirmation.

Graphs for lead and tungsten demonstrated the reliability of portable XRF data compared to the laboratory analysis.

The EPA released guidance in May 2004 for developing and implementing monitoring programs at hazardous waste sites. This guidance document was written for site managers responsible for removal and remedial site activities. This may be accessed from the EPA Superfund website (www.epa.gov/superfund/action/guidance/index.htm#hazwaste) and is presented as a six-step framework that begins with the identification of monitoring objectives and carries through to the development of decision rules

Hand held XRF analyzer being used for in-situ field screening of soil sample.

(exit criteria) for terminating or continuing the site activity and its monitoring program. This document is not intended to specify the scale, complexity, protocols, data needs or investigation methods for meeting the needs of site-specific monitoring. Rather, it presents a framework that can be used to develop and implement scientifically defensible and appropriate monitoring plans that promote national consistency and transparency in the decision-making process.

Further considerations

Although tungsten was originally believed to be insoluble in water, data from recent research has found otherwise. Therefore, potential migration of the metal on firing ranges exists. Large amounts of dissolved tungsten were found when tungsten powder was exposed to aqueous solutions, according to a Stevens Institute of Technology March 2002 report. The Toxic Substance Control Act (TSCA) Interagency Testing Committee nominated 20 tungsten compounds to the TSCA Priority Testing List (December 2003), published by the EPA in January 2004.

Knowing that tungsten is not the only compound found on a range, the Army has recommended further studies to better understand the potential interaction of tungsten with other metals. **PE**

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